



Recommendations on Fluorinated Pesticides

Massachusetts Sierra Club
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Summary

Synthetic organic pesticides have incorporated fluorine since their beginning in the 1940's. Some pesticides have included PFAS (per- and polyfluoroalkyl substances) since at least 1989. The active ingredients of several current pesticides are included in the [EPA PFAS Master list](#). Hundreds of other ingredients would be considered PFAS under various definitions. However, Responsible Industry for a Sound Environment (RISE), a U. S. pesticide industry group, recently denied that any "PFAS chemistry" was used in pesticides.¹

In 2020, MassDEP published standards for PFAS in drinking and ground water. This rule covers a subgroup of six related prevalent PFAS chemicals due to their high toxicity and persistence. One of them, PFOS, is the primary degradant of insecticide ingredients that were available to consumers until recently in Massachusetts. Numerous experts have called for regulating PFAS as a class.² The Massachusetts Sierra Club urges the Pesticide Board to further protect our "right to clean air and water" from PFAS and restrict all fluorinated pesticide products. These more than 2000 mostly General Use products account for over 12% of all products registered in Massachusetts.

History

Commercial fluorochemistry was developed in the 1940s. PFAS, a large and still growing group of synthetic fluorinated hydrocarbons, were commercially developed in the 1950's, and have found widespread use.³ The industry has known that PFAS (especially PFOA & PFOS) are toxic to mammals since at least 1978. The EPA

¹ E. A. Crunden and Ariel Wittenberg, "[Common mosquito pesticide packed with PFAS](#)", *E&E News*, March 26, 2021.

² Carol F. Kwiatkowski et al., "Scientific Basis for Managing PFAS as a Chemical Class", *Environ. Sci. Technol. Lett.* 2020, 7, 8, 532–543, June 30, 2020
<https://doi.org/10.1021/acs.estlett.0c00255>

³ https://www.3m.com/3M/en_US/pfas-stewardship-us/pfas-history/



became concerned about PFAS toxicological studies in 1998.⁴ EPA worked with industry to withdraw certain PFAS pesticides around 2000. The EPA issued its first PFAS health advisory in 2009.⁵

Synthetic organic pesticides have been in use since the 1940's. DDT's application as an insecticide was discovered in 1939 and released to the agricultural market in the U.S. in 1945. The next year, a fluorinated version of DDT that added one fluorine atom to each phenol group was invented apparently partly to circumvent the original patent.

The first fluoro-herbicide, trifluralin was invented in 1963 and remains one of the most widely used pesticides.⁶ The number of fluoro-pesticides have increased considerably since then. Today there are roughly 1200 active pesticide ingredients of which about 16% are fluorinated, and all but a few are organic compounds (e.g., sulfuryl fluoride). These pesticides fall into every category with herbicides, insecticides, and fungicides being the top three. About 300 have been given ISO names and are therefore most likely to be commercially available. The number of fluorinated compounds has been growing. In every year since 1998 "more than 50% of compounds with new ISO common names are fluoro-organic compounds."⁷

Chemistry

Most of these fluorinated pesticides also contain other halogens, usually chlorine. Only sixteen are brominated, a recent development in pesticide technology.⁸ Four contain both bromine and chlorine. Of these four, only two are registered in Massachusetts (Chlorfenapyr and Tralopyril) although both have several products per ingredient and are unrestricted (General Use). Chlorfenapyr and Tralopyril are similar chemicals and each contain a trifluoromethyl group (and chlorophenyl and cyanide groups). All halogens are dangerous in their gas form, which adds to the risks presented by manufacturing. Organofluorines all share the same basic chemical production processes (e.g., reliance on hydrogen fluoride, a highly

⁴ "Sharon Lerner, "3M Knew About the Dangers of PFOA and PFOS Decades Ago, Internal Documents Show" *The Intercept*, 2018.

<https://theintercept.com/2018/07/31/3m-pfas-minnesota-pfoa-pfos/>

⁵ EPA "2009 Provisional Health Advisory"

⁶ But banned in Europe since 2008 primarily due to high toxicity to aquatic life.

⁷ Yuta Ogawa et al., "Current Contributions of Organofluorine Compounds to the Agrochemical Industry", *iScience*, Volume 23, Issue 9, 25 September 2020.

⁸ Chlorfenapyr was the only one containing both fluorine and bromine in 2004.



dangerous chemical). Similar concerns are raised by the various phenol groups found in many of these pesticides.

The addition of fluorine (and other halogens) has added to pesticide potency, and increased duration of effect. The potency can derive from halogens' lipophilicity, and duration from chemical stability. These novel pesticides have been introduced to overcome pest resistance to simpler chemistries. Fluorine has generally been recognized as the most powerful of these halogens, which combined with the growing application and lowered costs of organofluorine chemistry, has led to its wide adoption.⁹ The downside is that potency and duration can lead to *bioconcentration*. These pesticides can also adhere to particles in water bodies which can first and most notably affect aquatic organisms. The stability in soil leads to greater if not unmanageable environmental *persistence*. All of this ultimately points to increased chemical burdens in humans and resulting harms to health.

PFAS Pesticide Products

The toxicity of a specific class of organofluorines, PFAS, has led to the application of some of them as pesticides. They include most notably three PFOS (C8) chemicals:

- Sulfluramid - From Dow Chemical and marketed nationally from 1989 until at least 2002. This general use consumer product was commonly applied against ants, cockroaches (S. C. Johnson Raid Max Roach Bait) and termites (Spectrum Spectracide). Still used in South America ("Mirex").
- Lithium perfluorooctane sulfonate (LPOS) - voluntarily withdrawn by 3M in 2000 due to environmental concerns. Still used in Japan as a consumer ant product ("Super Arinosu Korori").
- Flursulamid - Apparently used currently in China.

These three chemicals will degrade to PFOS in the environment. All are listed in EPA PFAS Master list.

PFAS groups are currently found in only a few pesticides.¹⁰ The following serve as the active ingredient in registered products in Massachusetts:

⁹ Peter Jeschke, "Latest generation of halogen-containing pesticides", *Pest Management Science*; vol. 73, p. 1053–1066, Feb. 2017.

¹⁰ One, Flubendiamide, has a pending EPA Notice to Cancel from 2016 due to "risks to aquatic invertebrates." The companies (Bayer and Nichino) would not agree to a voluntary withdrawal. No products in Mass. Source: <https://www.epa.gov/ingredients-used-pesticide-products/flubendiamide-notice-intent-cancel-and-other-supporting>



- Hexaflumuron — an insecticide with a polyfluorinated C2 branch + difluorobenzene. In commercial use since at least 1995 against termites. EPA Comptox even places this on the PFAS Master List of PFAS Substances (Version 2). 2 registered products.
- Metofluthrin — a pyrethoid with tetrafluorobenzene, which is considered a PFAS. 24 products including:
 - NuTone Haven Backyard Lighting & Mosquito Repellent System
 - OFF! Backyard Mosquito Repellent Coil - the instructions say “Works in semi-confined areas such as porches, patios and other areas where there is minimal breeze.” Also touted as “Metofluthrin [...] is safe and effective in warding off the pesky mosquitoes.”
 - Raid Bed Bug Foaming Spray
- Novaluron — an insecticide with two polyfluorinated groups. This pesticide is banned in the EU. 33 products.
- Noviflumuron — insecticide with a short-chain (C3) polyfluorinated group (and Difluorobenzene). Listed on PFAS Master List of PFAS Substances (Version 2). 4 products.
- Pyrifluquinazon — an insecticide that has short-chain (C3) perfluorinated group. Listed on PFAS Master List of PFAS Substances (Version 2). 2 products.
- Tefluthrin — a pyrethoid that contains tetrafluorobenzene, which is considered a PFAS. In use since at least 1989. 9 products.
- Tetraconazole — fungicide that contains a polyfluorinated C2 tetrafluoroethoxy branch (and dichlorobenzene). Listed on PFAS Master List of PFAS Substances (Version 2). 2 products. Used since at least 2001.

There are 89 products for these seven active ingredients. Each of the seven is in General Use (or in case of Tefluthrin have some products that are General Use).

Fluorinated Products

Another 76 organofluorine pesticides with less than seven fluorines have products registered in Massachusetts. These typically fall into the following categories of fluorination:

- A single fluorine atom including fluorobenzene (e.g., Fluoxastrobin or Flutriafol)
- Di- and trifluoromethyl groups. Some have two trifluoromethyl groups (such as Fipronil). Trifluoromethyl groups are the most frequent functional group (whereas for pharmaceuticals it is only one fluorine).¹¹

¹¹ Yuta Ogawa, *ibid*.



- Difluorobenzene (e.g., Cyflufenamid, which also has a trifluoromethyl group)
- Trifluorobenzene (e.g., Fluxapyroxad, which also has a difluoromethyl group)

While these less fluorinated chemicals do not fit the usual definition of PFAS, the European Union and some US states (such as legislation in New York) have adopted a broadened definition of PFAS that would include chemicals with at least one fully fluorinated carbon atom (such as CF₃).

All of these fluorinated ingredients represent about 2100 products that are registered for use in Massachusetts. This is over 13% of all Massachusetts products. Nearly all of these are general use (which is also typical of all active ingredients).

Environmental Risks

Since organofluorines are so rare in nature and very few natural or human processes can break the carbon-fluorine bond, it is also important to consider the risk from not only the pesticides themselves but also all their numerous human and animal metabolites and environmental degradants. For example, fipronil can first break down into the closely related Fipronil amide, Fipronil sulfone, Fipronil sulfide, and Desulfinylfipronil.¹² Each of these can break down combinatorially into further simpler chemicals. Agrochemicals with trifluoromethyl groups can produce trifluoroacetate (TFA) / trifluoroacetic acid (HTFA). HTFA, a strong, mildly toxic, and persistent acid is now accumulating in surface water, the atmosphere and rain.¹³ However, given the large number of active fluorinated ingredients, and that many of these products are understudied,¹⁴ the precautionary principle leads us to limit the use of all fluorinated products as a class to the maximum extent possible.

¹² Barbara J. Mahler, "Inclusion of Pesticide Transformation Products Is Key to Estimating Pesticide Exposures and Effects in Small U.S. Streams", *Environ. Sci. Technology* <https://dx.doi.org/10.1021/acs.est.0c06625>

¹³ David A. Ellis et al., "Thermolysis of fluoropolymers as a potential source of halogenated organic acids in the environment", *Nature*, Vol. 412, 19 July 2001, p. 321

¹⁴ This recent paper for example: "the molecular background behind the beneficial effect of fluorine [in agrochemicals] is often missing." Jianlin Han, "Chemical Aspects of Human and Environmental Overload with Fluorine", *Chemical Reviews*, 2020 (sec. 3.2) <https://dx.doi.org/10.1021/acs.chemrev.0c01263>



Recommendations

The Sierra Club has three interrelated recommendations for the Massachusetts Department of Agricultural Resources and Pesticide Board Subcommittee:

1. Suspend the registrations of existing pesticides that contain PFAS groups and not approve any new registrations.¹⁵
2. Suspend the registrations of all non-essential fluorinated pesticides and not approve any new registrations.
3. Classify any fluorinated products that the Subcommittee deems “essential” that are not already EPA Restricted as State Restricted Use (i.e., for certified applicators only).

Note that “essential” applications for fluorinated products would *exclude* for example crabgrass (e.g., Agway Spring Crabgrass Control) or backyard mosquito products or residential mouse products (e.g., Victor V Fast-Kill Brand Refillable Mouse Bait Station).¹⁶ Essential fluorinated products should also exclude those where a non-fluorinated alternative exists. For example, classes such as neonics and pyrethroids include numerous non-fluorinated products.¹⁷

¹⁵ There are EPA Registered PFAS ingredients that are not registered in Massachusetts such as Broflanilide and Lufenuron.

¹⁶ For a discussion of essentiality see:

Ian Cousins, “The concept of essential use for determining when uses of PFASs can be phased out”, *Environmental Science: Processes and Impacts*, May 2019.

¹⁷ Note that neither of the natural analogues that inspired these synthetic classes contains any halogens. (Pyrethrin does not contain a phenol group either.)